Supplementary information

Efficient synthesis of polycarbonate ether polyol via copolymerization CO_2 and 1,2-butylene oxide catalyst over layered Zn-Co double metal cyanide

Chen Liu [a,b], Yan Cao [a], Xianqiang Zeng [a], Zheng Zheng [a], Ziqiang Han [a], Peng He [a], Liguo Wang *[a,c]

[a] CAS Key Laboratory of Green Process and Engineering, National Engineering Research Center of Green Recycling for Strategic Metal Resources, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China

[b] School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250000, China

[c] School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

* Corresponding Author. E-mail: lgwang@ipe.ac.cn (L.G. Wang)

Characterization methods

FTIR result was obtained by a Nicolet 6700 Flex FTIR spectrometer using the standard KBr disc method of 4000 to 500 cm^{-1}. XPS analysis was performed on an X-ray photoelectron spectrometer with monochromatic Al Ka (hv =1486.6 eV). Scanning electron microscopy (SEM) images were obtained on Hitachi-S4800 scanning electron microscope, the sample was placed on the sample table about 10-15cm away from the evaporation source for rotation and gold spraying (10 KV 60 s). A Brucker D8 Advance X-ray diffractometer was used for wide-angle diffraction testing of the samples. The scanning range was 5-90° and the scanning rate was 5 °/min. TEM images were obtained using a high-resolution field emission transmission electron microscope (FEI Tecnai G2 F20). N_2 physical adsorption isotherm was obtained by an adsorption apparatus (Micromeritics 3flex) at -196 °C. Before the measurements, the samples were vacuumized at 150 °C for 12 h. Brunauer-Emmolett-Teller (BET) equation was used to measure the specific surface area (S_{BET}), Use t-plot to determine The specific external surface area (S_{ext}). *In situ* FTIR analysis using Mettler-Toledo ReactIR 15 reaction analysis system, data analysis using ReactIR(7.1) software, spectral scanning interval of 30 s, absorption peaks of 1, 2-butylene Carbonate (BC) ν(C=O) at 1819 cm^{-1}, At 1752 cm^{-1} is the ν(C=O) absorption peak of carbonate units and at 1101 cm^{-1} is the ν(C-O) absorption peak of ether units. ^{1}H NMR and ^{13}C NMR data were obtained from Bruker AV500 using $CDCl_3$ as solvent. The amount of average molecular weight (M_n) and dispersity ($Đ$) of the samples were collected by gel permeation chromatography (GPC). The instrument model is Shimadzu LC20. The sample was dissolved in HPLC grade THF at a concentration of about 5 mg· L^{-1}. Calibration was performed using the polystyrene sample standard and measured at 1 mL/min flow rate at 35 °C. The DSC test was performed using a differential scanning calorimeter (TA DSC 250) under a nitrogen atmosphere. The sample was heated from -90 °C to 110 °C at a rate of 10 °C/min, cooled to -90 °C after stabilization, and then continued to be heated to 110 °C at a rate of 10 °C/min

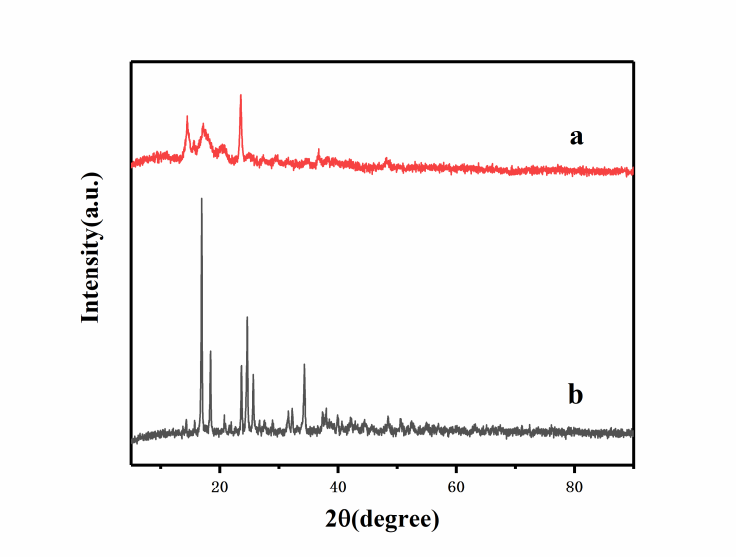

Fig. S1. X-ray powder diffraction patterns of (a) DMC, (b) L-DMC.

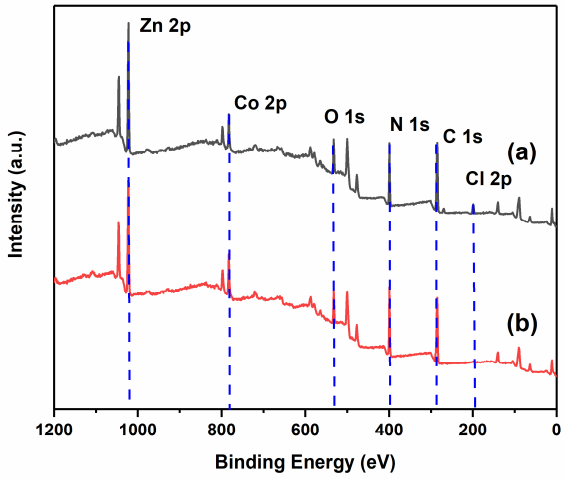

Fig. S2 XPS spectra of (a) DMC and (b) L-DMC.

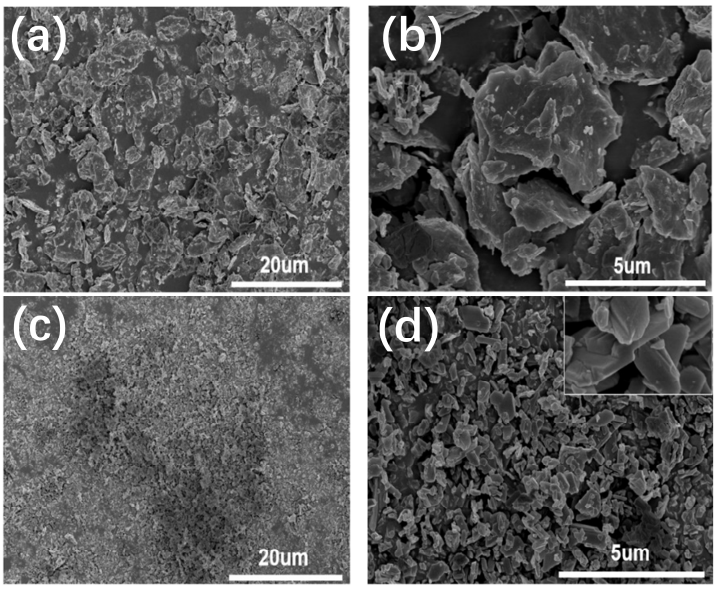

Fig. S3. SEM images (a, b) DMC, (c, d) L-DMC.

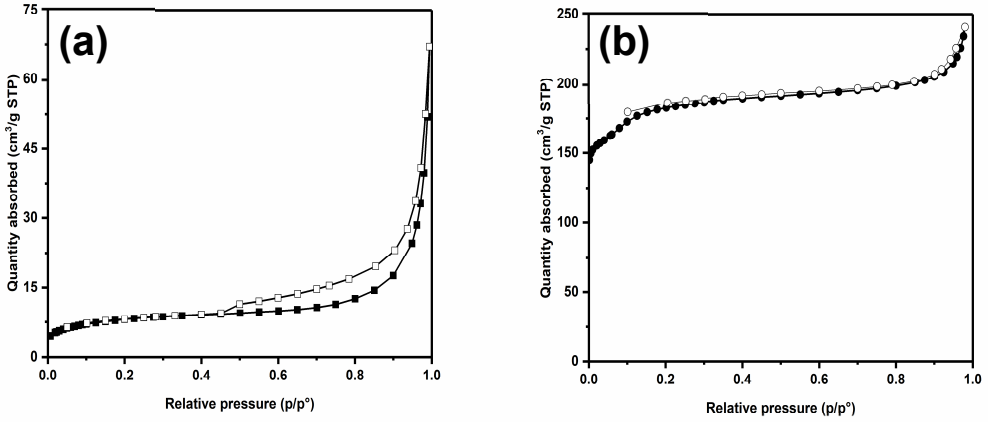

Fig. S4 Nitrogen physisorption isotherms of (a)DMC, (b)L-DMC.

Table S1.

Textural properties determined from N_2 physisorption of the DMC and L-DMC.

Catalyst	$S_{BET}(m^2/g)$	$S_{ext}(m^2/g)$
DMC	26	21
L-DMC	668	32

Table S2.

Influence of chain transfer agent type on the copolymerization of CO_2 and BO[a]

Entry	chain transfer agent	f_{CO2} [b] (%)	W_{BC} [b] (wt%)	M_n [c] (g/mol)	$Đ$ [c]	Productivity [d] (g polymer /g catalyst)
1	PPG-400	10.9	7.3	4800	2.2	413
2	1,4-BDO	30.3	8.2	10700	2.8	1239
3	SA	—	—	—	—	—
4	—	29.8	6.9	18300	2.3	1553

[a] Polymerization conditions: BO 10 mL, chain transfer agents 0.7 mmol, L-DMC 8.0 mg, 3 MPa, 110 °C, 4 h. [b] Determined by ^{1}H NMR and Formula (1), (2). [c] Determined by GPC.[d] Determined according to $W_{product}/W_{cat.}$

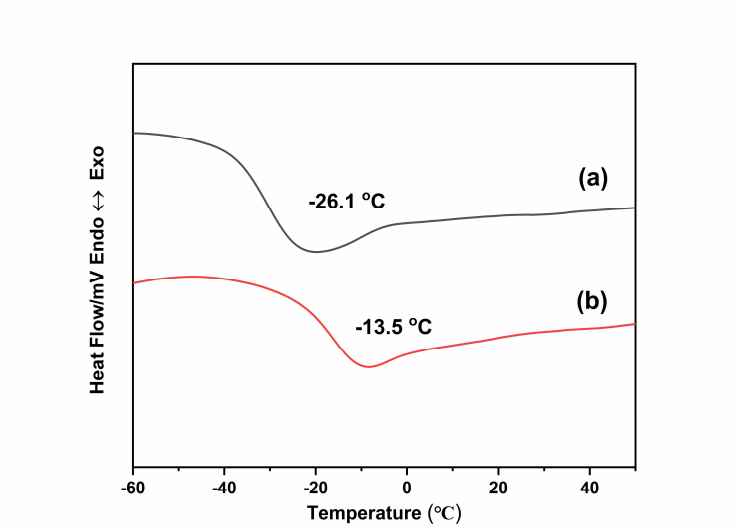

Fig. S5 DSC thermograms of the copolymerization of CO_2 and BO with different CO_2 incorporation fraction: (a) 18.0% (b) 30.3%.

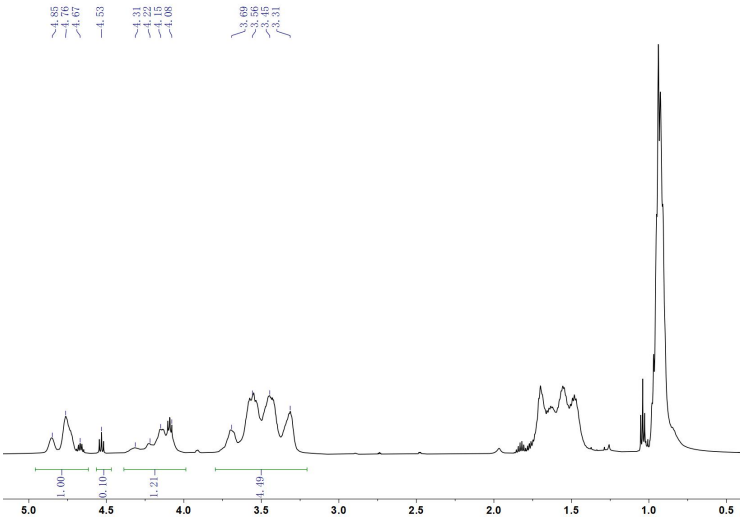

Fig. S6. ^{1}H NMR spectrum of polycarbonate ether polyol produced by L-DMC catalyst (entry 8, Table 1) in $CDCl_3$.

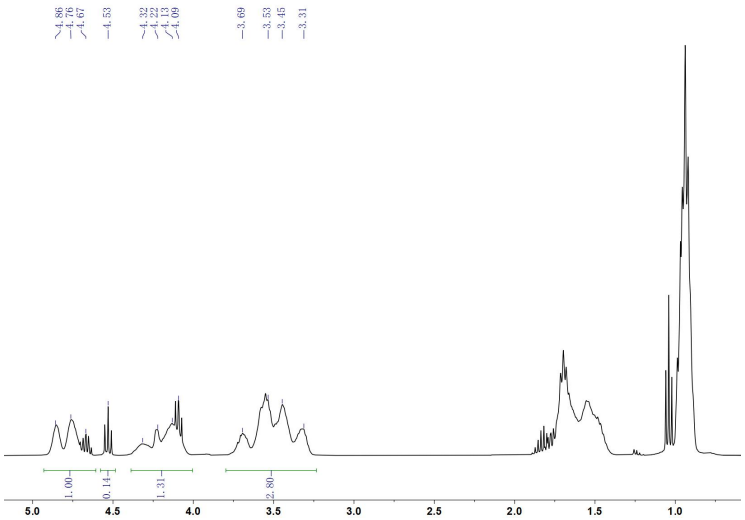

Fig. S7. ^{1}H NMR spectrum of polycarbonate ether polyol produced by L-DMC catalyst (entry 9, Table 1) in $CDCl_3$.

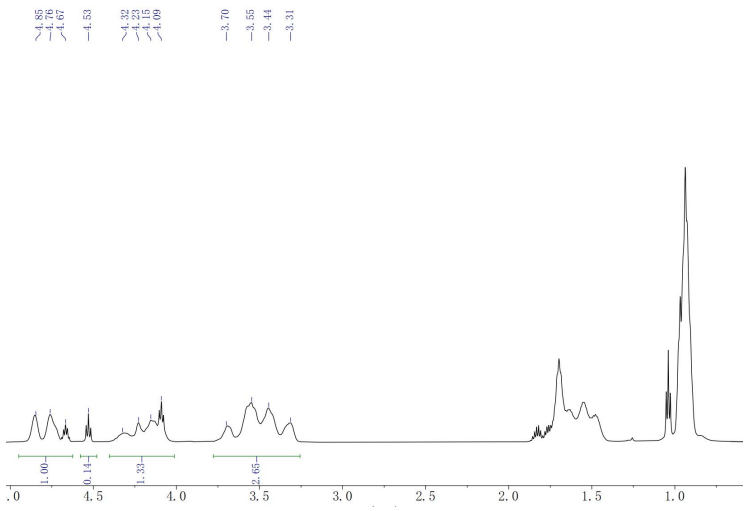

Fig. S8. ^{1}H NMR spectrum of polycarbonate ether polyol produced by L-DMC catalyst (entry 2, Table 1) in $CDCl_3$.

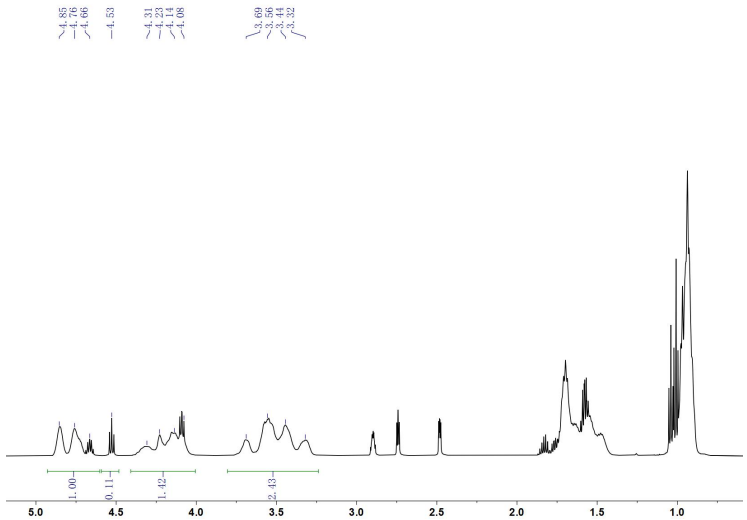

Fig. S9. ^{1}H NMR spectrum of polycarbonate ether polyol produced by L-DMC catalyst (entry 10, Table 1) in $CDCl_3$.

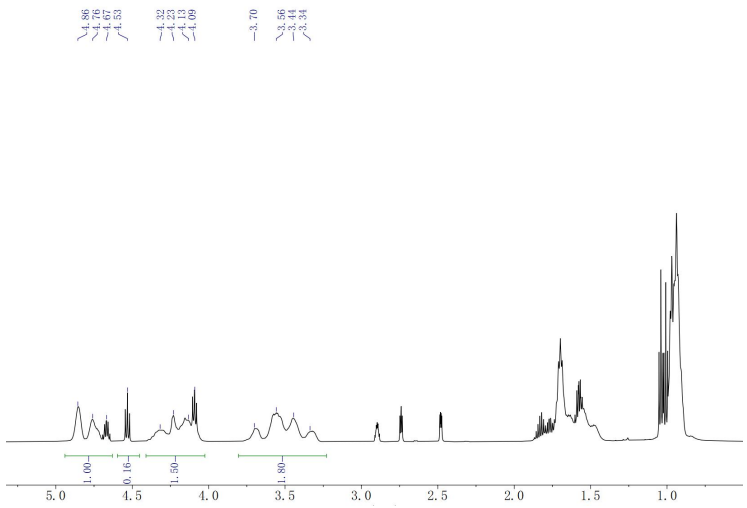

Fig. S10. ^{1}H NMR spectrum of polycarbonate ether polyol produced by L-DMC catalyst (entry 11, Table 1) in $CDCl_3$.

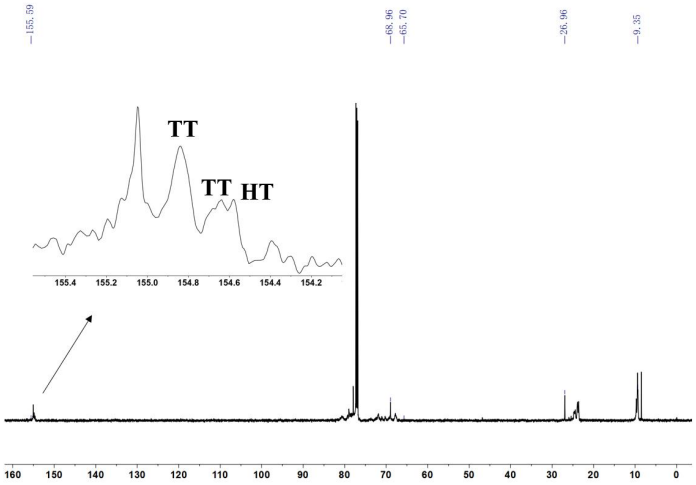

Fig. S11. ^{13}C NMR spectrum of polycarbonate ether polyol produced by L-DMC catalyst (entry 2, Table 1) in $CDCl_3$.

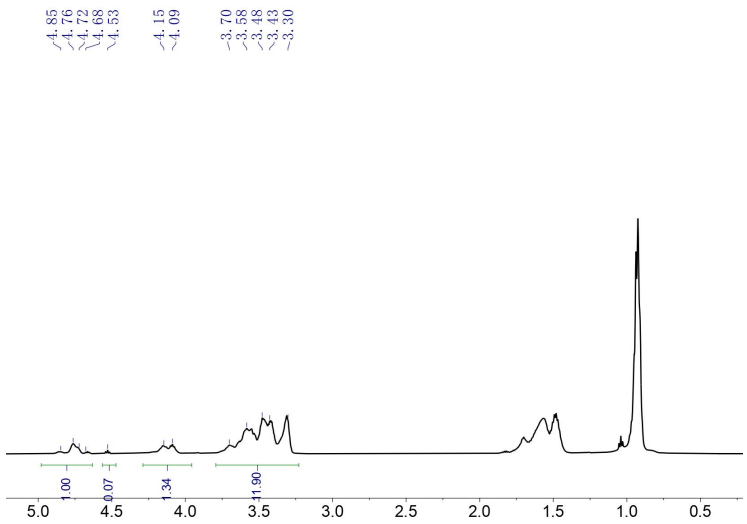

Fig. S12. ^{1}H NMR spectrum of polycarbonate ether polyol produced by DMC catalyst (entry 12, Table 1) in $CDCl_3$.

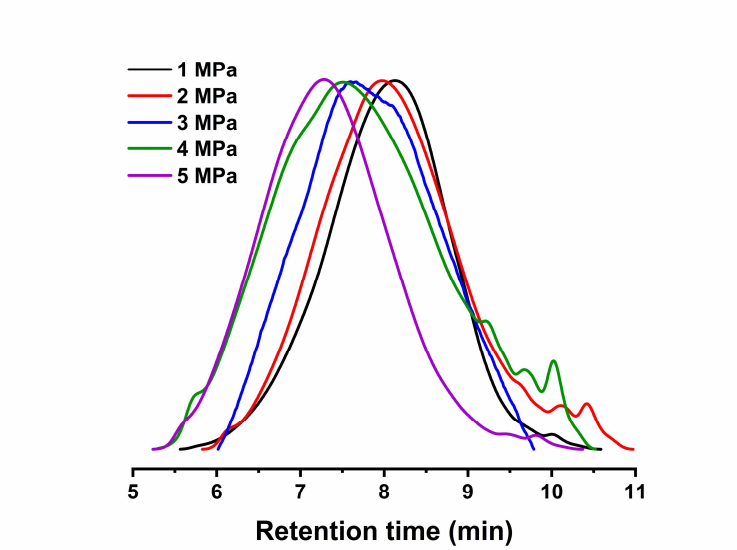

Fig. S13. the corresponding GPC traces of polycarbonate ether polyol (P_{CO2} = 1 MPa, 2 MPa, 3 MPa, 4 MPa and 5 MPa).

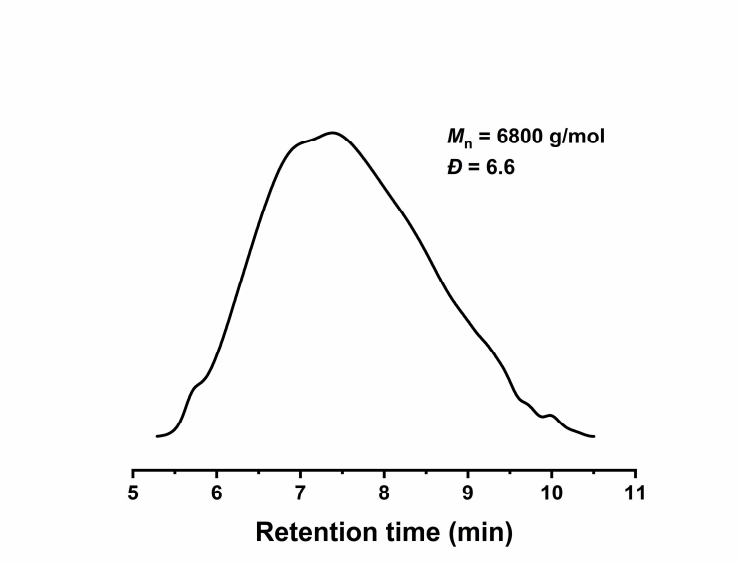

Fig. S14. the corresponding GPC trace of polycarbonate ether polyol (entry 3, Table 1).

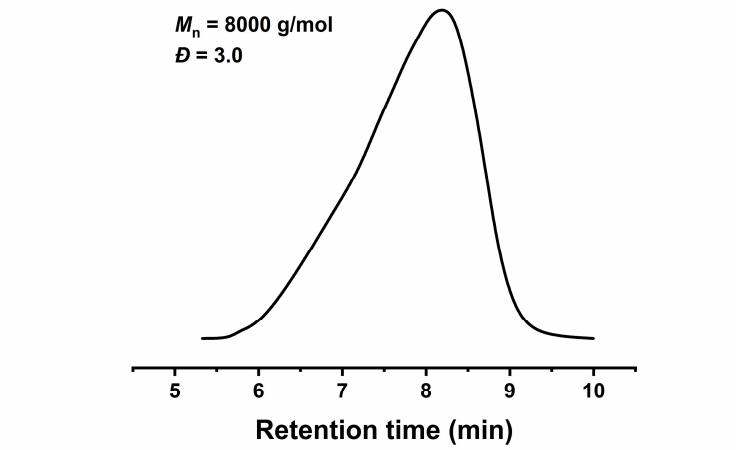

Fig. S15. the corresponding GPC trace of polycarbonate ether polyol (entry 6, Table 1).

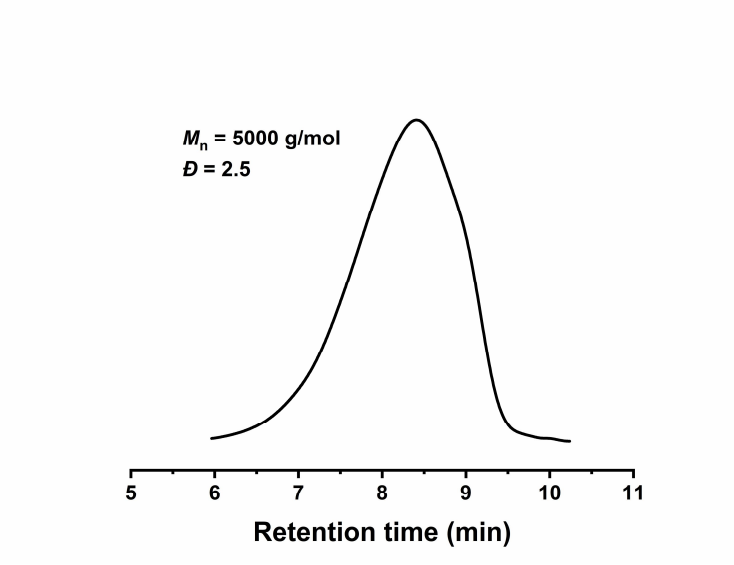

Fig. S16. the corresponding GPC trace of polycarbonate ether polyol (entry 12, Table 1).

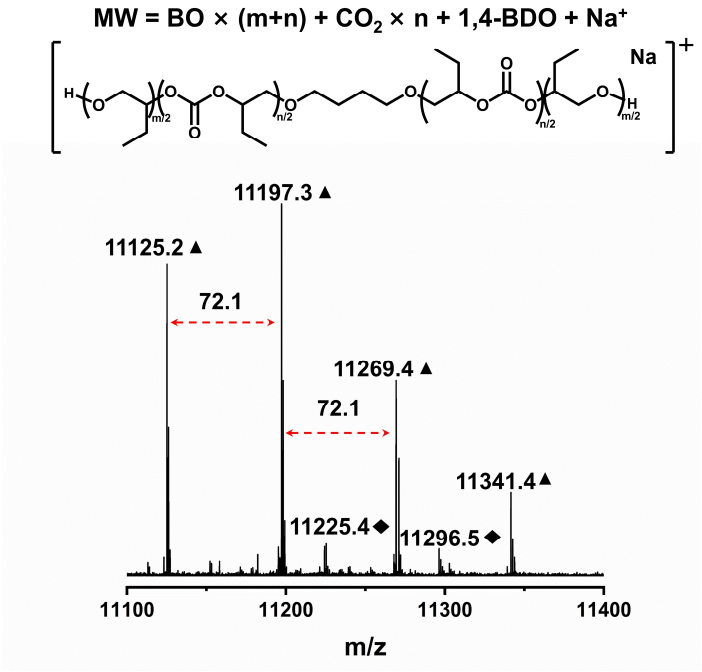

Fig. S17. MALDI-TOF MS spectrum of polycarbonate ether polyol catalyzed by L-DMC (entry 2, Table 1).